On the Equilibrium among Silicon in Molten Iron, Blast Furnace Slag and H_2-H_20 Mixed Gas. II : Investigation of the Equilibrium of the Reaction (Si0_2)_<Al_20_3-Ca0(sat.)>+2H_2=Si+2H_20

On the Equilibrium among Silicon in Molten Iron, Blast Furnace Slag and H_2-H_2O Mixed Gas. II
Investigation of the Equilibrium of the Reaction $(SiO_2)_{Al_2O_3\text{-}CaO(sat.)}+2H_2=\underline{Si}+2H_2O$*, **

Koji SANBONGI, Masayasu OHTANI and Hajime NAKAMURA

The Research Institute of Mineral Dressing and Metallurgy

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Synopsis

Using a CaO crucible, the equilibrium of the following reaction was studied under the conditions of $2CaO\cdot SiO_2$, $3CaO\cdot SiO_2$, or CaO saturation in the temperature range from 1,550° to 1,600°C:

$$(SiO_2)_{Al_2O_3\text{-}CaO(sat)}+2H_2=\underline{Si}+2H_2O. \quad (1)$$

The equilibrium constant of the reaction (I) becomes as follows:

$$K_{Si\text{-}H}=p^2_{H_2}\cdot a_{SiO_2}/p^2_{H_2O}\cdot \underline{Si}\%. \quad (2)$$

As was already reported in the previous paper, $K_{Si\text{-}H}$ is equal to $K^S_{Si\text{-}H}$. Thus, a_{SiO_2}*** in the molten SiO_2–CaO–Al_2O_3 ternary slag was calculated from the following equation:

$$a_{SiO_2}=K^S_{Si\text{-}H}\cdot \underline{Si}\%\cdot p^2_{H_2O}/p^2_{H_2}. \quad (3)$$

Finally, the authors determined the liquidus line of 1,550° and 1,600°C on the CaO side of SiO_2–CaO–Al_2O_3 ternary diagram from the equilibrium compositions of slag.

I. Introduction

Since the slag plays an important role in the iron and steel making process, many investigations have been performed on the properties of slag and the equilibrium between the slag and the molten iron from the viewpoints of physical chemistry or electrochemistry, but there still remain many unknown fields.

The authors studied the reduction equilibrium of silica in blast furnace slag to silicon in molten iron by H_2 as a series of a physico-chemical research in the iron making. In this system the reaction is expressed as follows:

$$(SiO_2)+2H_2 \rightleftarrows \underline{Si}+2H_2O. \quad (4)$$

In the previous paper(1) the reduction equilibrium of silica between SiO_2–CaO binary slag, saturated with SiO_2 or CaO and the molten iron was reported. Now, using a pure CaO crucible, the authors studied the reaction (4) of the system of SiO_2–CaO–Al_2O_3 slag, saturated with CaO in the temperature range from 1,550° to 1,600°C. In this case, the reaction are expressed as follows:

$$(SiO_2)_{Al_2O_3\text{-}CaO(sat.)}+2H_2 \rightleftarrows \underline{Si}+2H_2O. \quad (1)$$

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* The 37th report of the Research Institute of Mineral Dressing and Metallurgy.

** In this report, parenthesis and underline mean the component in slag and molten iron respectively.

*** a_{SiO_2} means the activity of SiO_2 in molten slag.

(1) K. Sanbongi and M. Ohtani, Sci. Rep. RITU, A 4 (1952), 59.

II. Consideration from viewpoint of the phase rule on the equilibrium

In the previous paper, the authors considered the freedom of the system in which SiO_2–CaO binary slag takes part, from the viewpoint of the phase rule. In this section, the authors considered the freedom of the system in which the molten SiO_2–CaO–Al_2O_3 is saturated with CaO.

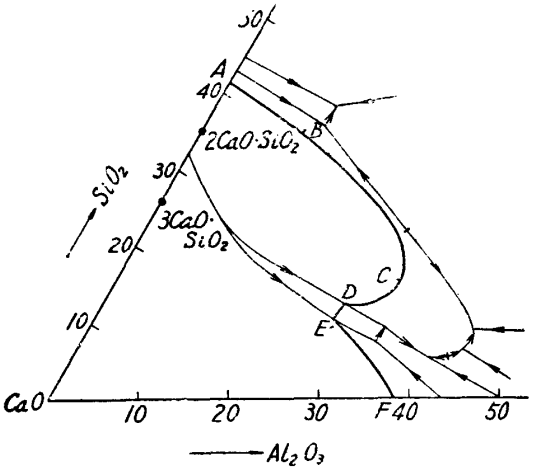

Fig. 1 CaO side in the equilibrium diagram of SiO_2–CaO–Al_2O_3 system.

The liquidus line of CaO side in the equilibrium diagram of SiO_2–CaO–Al_2O_3 system[2] at 1,600°C is shown in Fig. 1 in which the curve ABCD is the liquidus of $2CaO \cdot SiO_2$, the range of saturation by this compound, and the freedom F becomes 4 from the phase rule. The range DE is the liquidus of $3CaO \cdot SiO_2$ and F becomes 4.

Finally, the range EF is the liquidus of CaO and F also becomes 4. On the whole range of ABCDEF, therefore, the freedom becomes 4, that is,

$$f(T, P, p_{H_2}/p_{H_2O}, CaO/SiO_2, \underline{Si}, Al_2O_3) = 0,$$

$$N_{SiO_2} + N_{CaO} + N_{Al_2O_3} = 1.$$

Fig. 2 shows the space model of this system at the constant pressure. Curve $B_1'B_2$ shows the relation among $\underline{Si}$%, p_{H_2}/p_{H_2O} and SiO_2–CaO binary slag saturated with $2CaO \cdot SiO_2$, under the condition of T_1 and P. Then $T_1'T_2$ shows the relation among $\underline{Si}$%, p_{H_2}/p_{H_2O} and SiO_2–CaO–Al_2O_3 slag, saturated with $2CaO \cdot SiO_2$ at the same temperature. Further, lines a, b and c give respectively the relation between $\underline{Si}$% and SiO_2% in slag saturated with CaO, corresponding to a given ratio of p_{H_2}/p_{H_2O}. From this model it is evident that $\underline{Si}$% so much increases as the ratio of p_{H_2}/p_{H_2O} becomes large under a given composition of slag and decreases as SiO_2 content in slag becomes low under the condition of the constant temperature and pressure. In this system, therefore, even if T, P and ratio p_{H_2}/p_{H_2O} are determined, $\underline{Si}$% can not be determined, but CaO/SiO_2 must be determined to establish the equilibrium state.

III. Experimental apparatus and procedure

The essential part of the apparatus was already descrived in the previous paper,[1] so that the authors supplement only some improved points.

(2) N. L. Bowen and J. W. Greig, Amer. J. Sci., **13** (1927), 35; F. Körber and W. Oelsen, Stahl u. Eisen, **60** (1940), 921; W. Jander and E. Hoffmann, Phys. Chem. Silikate, (1941), 565.

a) Temperature measurement

Hitherto, the temperature was measured by the optical pyrometer which had previously been calibrated. In this experiment an indicator, which is very sensible to changes in temperature, was used together with the former.

In other words, when the sample was melted in a high frequency induction furnace, the change of flux, which was due to the change of voltage, was caught by a turn of a copper wire settled under the induction coil, then amplified by the tube, UZ-30, and detected by the microammeter. The change in the current recorded on the microammeter was very sensible.

b) Used slag

Since the transition of liquidus line of CaO side on the SiO_2–CaO–Al_2O_3 diagram in the range from 1,550° to 1,600°C was small, four compositions of slag, shown in Table 1 were used in all experiments.

Table 1. Compositions of used slags.

	SiO_2%	CaO%	Al_2O_3%
S-1	34.9	54.2	9.9
S-2	26.1	54.4	19.4
S-3	19.0	54.9	25.7
S-4	10.2	63.7	28.9

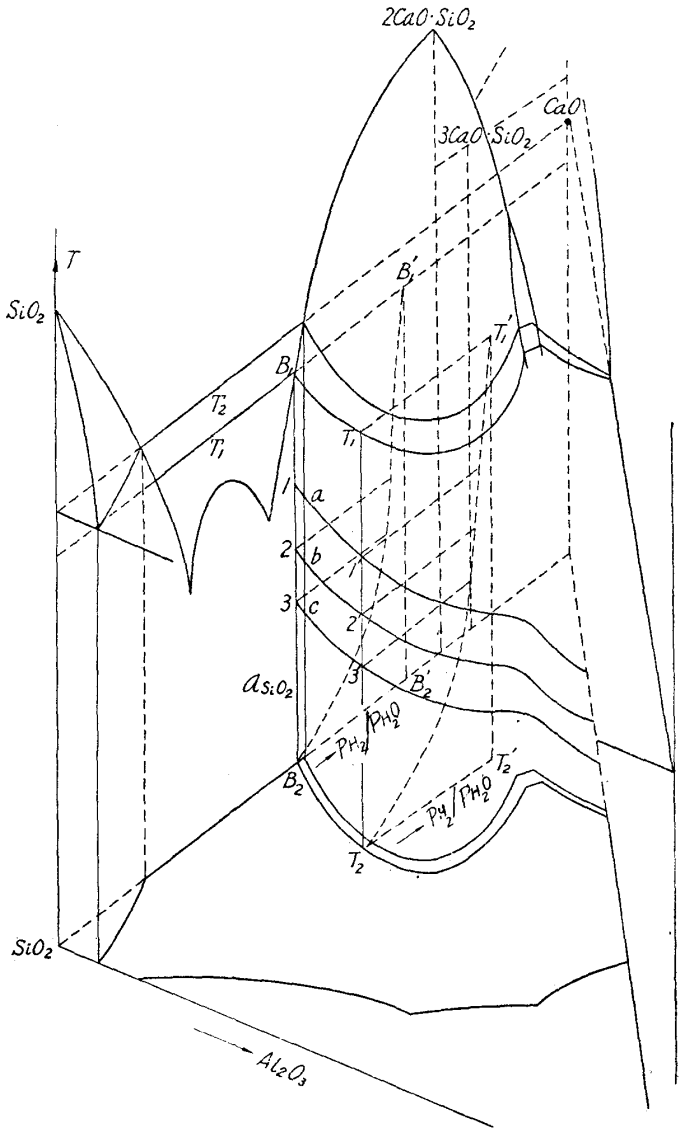

Fig. 2 Space model of equilibrium. (at constant pressure)

IV. Experimental results

Experimental results are summarized in Table 2. Slag compositions in Table 2 are the equilibrium composition at each temperature. So, these values correspond to the composition on the liquidus line of SiO_2–CaO–Al_2O_3 diagram. Now, plotting compositions of these slags on SiO_2–CaO–Al_2O_3 ternary diagram, liquidus lines shown in Fig. 3 were obtained at each temperature. As was already described in the introduction, the general equation of the reduction of SiO_2 in the slag expressed as follows:

$$(SiO_2)+2H_2 \rightleftarrows \underline{Si}+2H_2O\,. \qquad (4)$$

The authors already determined temperature function of equilibrium constant for the system, saturated with SiO_2 or CaO as follows:

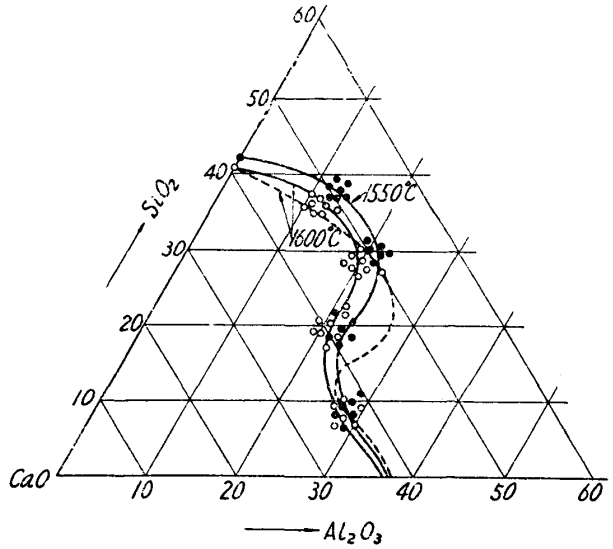

Fig. 3 Liquidus lines at 1,550° and 1,600°C of CaO side of SiO_2–CaO–Al_2O_3 ternary system.

$$(SiO_2)_{(sat.)}+2H_2 \rightleftarrows \underline{Si}+2H_2O, \qquad (5)$$

$$K^{S}_{Si\text{-}H}=p^2_{H_2}/p^2_{H_2O}\cdot \underline{Si}\%\,, \qquad (6)$$

$$\log K^{S}_{Si\text{-}H}=12{,}800/T-3.62. \qquad (7)$$

Furthermore, from the experimental results on the equilibrium of the reaction (5), it was recognized that the relation between Si% and $p^2_{H_2}/p^2_{H_2O}$ would be shown by a straight line at a given temperature, and that the activity coefficient of Si would be a constant under about 8% Si.

From the above results, the equilibrium constant of the

Table 2. Experimental results.

Heating No	p_{H_2}/p_{H_2O}	Holding time (mins.)	Si%	Si% (equil.)	Initial Si%	SiO_2%	CaO %	Al_2O_3%
				1,550°C				
2T. 101	71.35	60	0.27		0.50	38.0	48.2	12.9
〃 102	〃	50	0.31	0.30	〃	37.9	47.9	11.6
〃 109	〃	60	0.30		〃	38.5	48.5	12.8
〃 104	81.63	50	0.56	0.56	0.70	37.7	48.7	11.0
〃 105	〃	60	0.56		〃	38.5	48.1	12.6
〃 106	93.57	60	0.79		0.90	36.6	50.9	11.6
〃 108	〃	50	0.85	0.82	〃	37.9	48.0	11.9
〃 110	〃	40	0.82		〃	36.1	48.2	12.3
2T. 202	71.35	50	0.28		0.40	31.8	48.5	18.6
〃 210	〃	50	0.29	0.29	〃	32.0	48.2	19.7
〃 201	〃	60	0.30		〃	31.3	49.4	19.9
〃 203	81.63	60	0.52	0.53	0.60	30.2	49.9	20.2
〃 208	〃	50	0.55		〃	30.4	47.4	19.3
〃 205	93.57	60	0.69	0.71	0.80	30.3	46.2	20.6
〃 207	〃	50	0.73		〃	29.2	48.5	21.2
2T. 301	71.35	60	0.21	0.21	0.30	18.2	58.1	22.4
〃 302	〃	50	0.21		〃	19.4	57.4	21.2
〃 303	81.63	50	0.53	0.52	0.50	20.1	57.5	23.6
〃 307	〃	60	0.51		〃	21.1	58.9	19.4
〃 305	93.57	50	0.60	0.60	0.70	19.5	60.7	19.7
〃 308	〃	40	0.61		〃	17.5	57.9	22.8
2T. 407	93.57	60	0.03	0.03	0.15	9.2	66.5	23.4
〃 408	〃	40	0.03		〃	7.2	67.2	24.6
〃 403	107.5	60	0.05	0.06	0.25	5.0	66.4	27.5
〃 404	〃	50	0.06		〃	5.3	65.2	29.8
〃 405	123.7	60	0.16	0.16	0.35	6.1	63.8	28.9
〃 406	〃	50	0.15		〃	7.7	68.3	20.0

Table 2. Experimental results. (continued)

1,600°C

Heating No	p_{H_2}/p_{H_2O}	Holding time (mins.)	Si%	Si% (equil.)	Initial Si%	SiO_2%	CaO%	Al_2O_3%
1T. 102	54.81	50	0.31		0.35	36.5	54.0	9.1
〃 105	〃	40	0.26	0.29	〃	37.4	50.7	9.3
〃 106	〃	60	0.27		〃	36.8	52.8	9.7
〃 108	71.35	60	0.65		0.60	36.2	52.8	9.3
〃 114	〃	60	0.62	0.63	〃	36.7	49.5	12.1
〃 116	〃	50	0.64		〃	37.6	49.3	11.3
〃 112	81.63	50	0.74		0.80	37.5	49.8	9.7
〃 113	〃	40	0.69	0.72	〃	37.8	49.0	11.5
〃 117	〃	60	0.72		〃	37.2	50.5	9.8
〃 118	93.57	60	1.01		1.20	36.9	50.5	13.1
〃 119	〃	50	1.05	1.01	〃	37.6	49.3	12.3
〃 120	〃	40	0.99		〃	37.7	50.7	10.9
1T. 203	54.81	60	0.36	0.35	0.35	29.5	50.3	20.0
〃 219	〃	50	0.34		〃	28.7	52.4	18.4
〃 215	71.35	60	0.39	0.40	0.60	29.6	48.7	21.5
〃 216	〃	50	0.41		〃	26.3	46.1	28.1
〃 208	81.63	60	0.62	0.62	0.80	26.4	52.7	19.9
〃 209	〃	50	0.61		〃	28.8	50.5	20.6
〃 212	93.57	60	1.13	1.14	1.20	29.4	50.5	20.2
〃 214	〃	50	1.16		〃	29.8	52.4	17.4
1T. 301	93.57	60	0.68		0.90	21.1	58.8	18.0
〃 303	〃	55	0.71	0.69	〃	21.6	54.0	23.8
〃 304	〃	50	0.69		〃	19.0	56.7	24.2
〃 305	81.63	60	0.57		0.70	21.9	55.8	20.8
〃 307	〃	50	0.53	0.57	〃	17.4	65.1	18.3
〃 308	〃	46	0.59		〃	17.4	55.2	26.6
〃 311	71.35	60	0.33	0.31	0.50	15.7	67.5	19.7
〃 314	〃	50	0.30		〃	19.9	53.9	25.7
〃 316	54.81	60	0.20		0.30	18.9	53.8	23.3
〃 317	〃	50	0.19	0.20	〃	23.7	55.5	19.9
〃 318	〃	45	0.21		〃	21.8	55.2	22.5
1T. 401	54.81	60	0.01	0.02	0.10	10.2	62.5	27.5
〃 402	〃	50	0.02		〃	9.0	60.6	29.4
〃 404	93.57	60	0.03	0.03	0.20	8.9	64.0	27.5
〃 415	〃	50	0.02		〃	7.8	61.5	29.4
〃 410	107.5	50	0.04	0.05	0.30	6.8	63.9	27.9
〃 411	〃	40	0.05		〃	6.6	65.1	27.8
〃 412	123.7	60	0.18	0.18	0.40	6.5	64.9	26.9
〃 414	〃	40	0.17		〃	6.1	64.8	27.7

reaction (I) can be expressed as follows:

$$K_{Si\text{-}H}=p^2_{H_2}\cdot a_{SiO_2}/p^2_{H_2O}\cdot \underline{Si}\% . \quad (2)$$

If the activity of pure β-cristobalite is a unity, $K_{Si\text{-}H}$ becomes equal to $K^S_{Si\text{-}H}$ at a given temperature. Thus,

$$a_{SiO_2}=K^S_{Si\text{-}H}\cdot \underline{Si}\%\cdot p^2_{H_2O}/p^2_{H_2} . \quad (3)$$

Since the value of $K^S_{Si\text{-}H}$ can be calculated from equation (7) at each temperature, if Si% and p_{H_2}/p_{H_2O} obtained in this experiment are introduced in the equation (3), a_{SiO_2} ought to be calculated for each slags. Thus calculated values of a_{SiO_2} of used slags at the temperatures 1,550° and 1,600°C are shown in Table 3.

Successively, the establishment of the following equilibrium was concluded in

molten SiO_2–CaO–Al_2O_3 slag corresponding to the slag compositions:

$$2CaO{\cdot}SiO_2(s) \rightleftarrows 2CaO(l) + SiO_2(l), \quad (8)$$

$$3CaO{\cdot}SiO_2(s) \rightleftarrows 3CaO(l) + SiO_2(l), \quad (9)$$

$$CaO(s) \rightleftarrows CaO(l). \quad (10)$$

Table 3. Values of activity of SiO_2.

Temperature °C	Kinds of Slags	SiO_2%	CaO%	Al_2O_3%	a_{SiO_2}
1,550	S–1	37.7	48.6	12.1	0.21
	S–2	30.7	48.3	19.9	0.20
	S–3	19.3	58.4	21.5	0.15
	S–4	8.4	63.1	27.5	0.02
1,600	S–1	37.3	50.1	11.3	0.20
	S–2	29.3	51.4	19.8	0.20
	S–3	20.9	55.2	22.9	0.12
	S–4	8.4	63.1	26.8	0.01

Jander and Hoffmann[2] published that the rate of formation of these compounds was rapid and easily attained to the equilibrium. The authors examined the slag by the microscope and X-ray analyses and detected the existence of these compounds.

V. Considerations

a) The calculated values of the activities of SiO_2

For the activities of SiO_2 in the SiO_2–CaO binary slag, Murry and White[3] already calculated from the dissociation constant, and Rey[4] calculated by the combination of heat of formation, heat of solution and the liquidus line of FeO–SiO_2 equilibrium diagram. Further, Chang and Derge[5] measured the potential of the following reversible cell:

$$SiC \mid \begin{matrix} SiO_2\text{–}CaO \\ SiO_2\text{–}CaO\text{–}Al_2O_3 \end{matrix} \mid C,$$

and calculated the values of a_{SiO_2} for several concentrations of SiO_2 in slags from the relation between the electromotive force and a_{SiO_2} at the temperature from 1,550° to 1,650°C.

In comparing these results with the authors' calculated values of a_{SiO_2} for SiO_2–CaO binary solution, the results of Murry and White[3] and Rey[4] showed some difference, but the results of Chang and Derge[5] for SiO_2–CaO agreed very well with the authors' values, as already described in the previous paper.[1]

Since values of a_{SiO_2} for SiO_2–CaO–Al_2O_3 slags proposed by Chang and Derge[5] were those for homogeneous SiO_2–CaO–Al_2O_3 solution, they could not directly coincide with authors' values of a_{SiO_2}, which were calculated for SiO_2–CaO–Al_2O_3 slag saturated with CaO. But the authors' values almost agreed with the extraporated values from the data of Chang and Derge.[5]

(3) P. Murry and J. White, Discussions of Faraday Society, (1948) No. 4 287.
(4) M. Rey, ibid. 257.
(5) L. C. Chang and G. Derge, Trans. A. I. M. E., T. P., (1946), 2101.

b) The liquidus line of CaO side

The equilibrium diagram of SiO_2–CaO–Al_2O_3 were already proposed by some investigators.[2] But the liquidus lines of CaO side in the composition range from 12% to 25% SiO_2 in these diagram did not coincide with each other. One of the reasons for such a discrepancy may be found in the disintegration of slag. So the sampling of slag for chemical analyses was performed with special attention.

Further, slags were examined under microscope and with X-ray analysis, and although the formura of compound were not detected, the existence of some compounds was recognized.

Summary

1) Using a pure CaO crucible, the authors estimated the equilibrium of the following reaction in the temperature range from 1,550° to 1,600°C:

$$(SiO_2)_{Al_2O_3\text{-}CaO(sat.)} + 2H_2 \rightleftarrows \underline{Si} + 2H_2O\,.$$

Then the activity of SiO_2 in molten SiO_2–CaO–Al_2O_3 slag saturated with $2CaO{\cdot}SiO_2$, $3CaO{\cdot}SiO_2$ and CaO, were calculated.

2) Making the space model of this equilibrium state, the authors illustrated the relation of the equilibrium among silicon in molten iron, molten SiO_2–CaO–Al_2O_3 ternary slag and H_2–H_2O mixed gas.

3) The authors deterimned the liquidus line of CaO side in SiO_2–CaO–Al_2O_3 ternary system under the existence of molten iron phase.

In conclusion, the authors wish to extend their hearty thanks to Professor Matoba for his guidance, to Professor Takeuchi for his assistence in the examination under microscope and with X-ray, and to Mr. Obinata for his generous assistance.

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